

PHOTOCATALYTIC DEGRADATION OF CHLORPYRIFOS IN WATER USING TITANIUM DIOXIDE AND ZINC OXIDE

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ABSTRACT

In the present work, degradation of chlorpyrifos in water was investigated using semiconductor oxide catalysts, i.e. zinc oxide (ZnO) and titanium dioxide (TiO₂). The influence of various parameters, such as type of the catalyst, irradiation time, catalyst concentrations, pH, and sodium bicarbonate salt was also studied. Results indicated that the optimal concentration of the catalyst was 0.15 g/L. It was also found that TiO₂ is a better catalyst than ZnO under the same photocatalytic reaction conditions. The highest removal efficiency was achieved at pH 9. Results from the present study suggested that the photodegradation efficiency of pesticides increases with the increase of the illumination time. The photodegradation efficiency of chlorpyrifos was found to be 80% and 90% for UV/ZnO and UV/TiO₂, respectively. Photodegradation in the presence of sodium bicarbonate was slower in comparison to that without the salt. In addition, the efficiency of photocatalytic degradation in distilled water was higher than in natural water.

KEYWORDS: photocatalytic degradation, chlorpyrifos, titanium dioxide, zinc oxide.

1 INTRODUCTION

Pesticides are extensively used in agriculture, gardening, and a wide variety of other household applications. Chlorpyrifos is an organophosphorous insecticide which was used for controlling insect pests in soil, ornamental plants, fruits, and vegetables worldwide [1]. In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of semiconductor photocatalysts (e.g., TiO₂ and ZnO), an energetic light source, and an oxidizing agent, such as oxygen or air [2]. The positive hole either oxidizes the pollutant directly or it oxidizes water to produce hydroxyl radicals ([•]OH), whereas the electron in the conduction band reduces the oxygen adsorbed on the photo-

catalyst (TiO₂ or ZnO) [3]. In the degradation of organic pollutants, the hydroxyl radical is generated from the oxidation of adsorbed water, where it is adsorbed as OH⁻, the primary oxidant, and the presence of oxygen can prevent the recombination of an electron hole pair. The [•]OH attacks organic compounds, such as pesticides, chlorinated aromatics, and nitro phenols. TiO₂ and ZnO, especially in the recent years, are used as effective, inexpensive, nontoxic semiconductor photocatalysts for the degradation of a broad range of organic chemicals [4]. Due to its stability and non-toxicity, titanium dioxide (TiO₂) has proved to be an excellent catalyst, and its behavior is very well-documented in literature [5]. However, the photocatalytic effect of other semiconductors like zinc oxide (ZnO) is not so well understood. ZnO is a very interesting, wide-band-gap semiconductor material, mainly because of its direct band gap, large excitation binding energy, and piezoelectric properties. The band gap of this semiconductor material is ca. 3.2 eV, which corresponds to a radiation wavelength of around 390 nm. Therefore, an UV light with a wavelength shorter than 380 nm is needed to excite the electrons in valence band to conduction band [6-8]. Few studies on photocatalytic oxidation process of pesticides exist [9-12]. The main objective of the present work was to study the photocatalytic degradation of chlorpyrifos in water using TiO₂ and ZnO under UV light. The influence of the catalyst concentration, type of catalyst, pH, and NaHCO₃ concentration was studied.

2 MATERIALS AND METHODS

The ZnO catalyst was purchased from FLUKA. The diameter, specific surface area, and band-gap energy of ZnO were 14 nm, 10 m².g⁻¹, and 2.92 eV, respectively. Titanium dioxide (TiO₂ Degussa P25) had a surface area of 55 m²/g. Chlorpyrifos was purchased from Supelco, while NaOH and HNO₃ were obtained from Merck Co., Germany. The reaction solution (i.e. sodium bicarbonate, NaHCO₃) was also purchased from Merck Co., Germany. The concentration of chlorpyrifos in the samples was 6 mg.L⁻¹ (we also used 30% insecticide). The samples were adjusted in the reactor at 5 different retention times of 5, 10, 15, 20, and 25 min. The pH of the samples was in the range of 5-9

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(i.e. 5, 7, and 9). The reaction temperature was kept at 25 ± 1 °C. In the present work, samples were synthesized from deionized water.

For the photodegradation of chlorpyrifos, a solution containing a known concentration of the pesticides and ZnO or TiO₂ was prepared and was allowed to equilibrate for 30 min in the darkness. Then, 50 ml of the prepared suspension was transferred to a 800-ml Pyrex glass reactor. Irradiation was carried out with a 125- W medium pressure mercury lamp (Philips, Holland), which was placed above the batch photo reactor. The distance between the solution and the UV source was kept constant (3.75 cm) in all experiments. The light intensity at the surface of the solution was 80 W m^{-2} , which was measured by a Hagner detector (EC1- UV-C, Sweden). The pH of the solution was adjusted with HNO₃ or NaOH. The pH values were measured by a pH-meter (Sartorius, Germany). Afterwards, the lamp was switched on to initiate the reaction. During the irradiation, agitation was maintained by a magnetic stirrer (IKA-Werke, Germany) to keep the suspension homogeneous, and the suspension was sampled after an appropriate illumination time. The temperature was kept at 25 ± 1 °C by circulating water in a double jacket cooling array. The dispersive liquid-liquid microextraction (DLLME) technique was used for the extraction of chlorpyrifos [13].

Five ml of the sample (water + analyte) was mixed with 500 ml of the extraction solution (2 ml internal standard: malathion 1000 mg L^{-1} , 10 ml chloroform, and 100 ml acetone). The mixture was then centrifuged for 5 min at 3500 rpm. After this process, the upper aqueous phase and the droplets precipitated at the bottom of the conical test tube were collected by a pipette and 1 ml of it was analyzed using a GC-MS combination (Varian CP-3800 GC with MS trap detector Varian Saturn 2200, run in EI mode) to perform the chemical analysis and identify the chemical compounds. Injector temperature was 270 °C, and analysis was carried out using a capillary column (Varian DB-5 column; 30 m x 250 μm I.D., film thickness 0.25 μm). The method started at 150 °C, which was held for 2 min, then ramped to 120 °C at a rate of 25 °C/min, followed by a temperature increase to 270 °C (held for 2 min). The method used a split ratio of 1:10 helium (99.999%), which was used as carrier gas at 1 ml/min. Statistical analyses (T-test and one-way ANOVA) were performed using SPSS software.

3 RESULTS AND DISCUSSION

3.1 Effect of catalyst dosage

The effect of the catalyst dosage (both for TiO₂ and ZnO) on the photodegradation efficiency is shown in Figs. 1 and 2. The photodegradation efficiency increased with increasing concentration of the photocatalyst, reached the highest value at 0.15 g/L, and then decreased. It is believed that the increase in the number of TiO₂ and ZnO particles will increase the number of both photons and

chlorpyrifos molecules absorbed. Therefore, the degradation efficiency can be enhanced with increasing catalyst concentrations, due primarily to the increase in the total surface area available for adsorbing the contaminant. A further increase of the catalyst concentration beyond 0.15 g/L may cause light scattering and screening effects. The excessive TiO₂ and ZnO photocatalyst concentrations lead to opacity of the suspension, which prevents the catalyst in the solution from being further illuminated [14]. The scattering and screening effects reduce the specific activity of the catalyst. At high catalyst concentrations, particle aggregation may also reduce the catalytic activity. Hence, the photodegradation efficiency of chlorpyrifos decreases. Similar results have been reported for degradation of methamidophos [15], dimethoate [16], and diazinon [9].

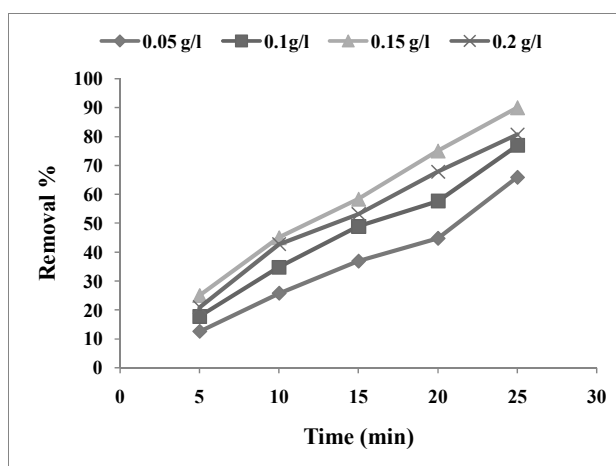


FIGURE 1 - Effects of TiO₂ dosage in UV/TiO₂ system (chlorpyrifos = 6 mg/L and pH=9)

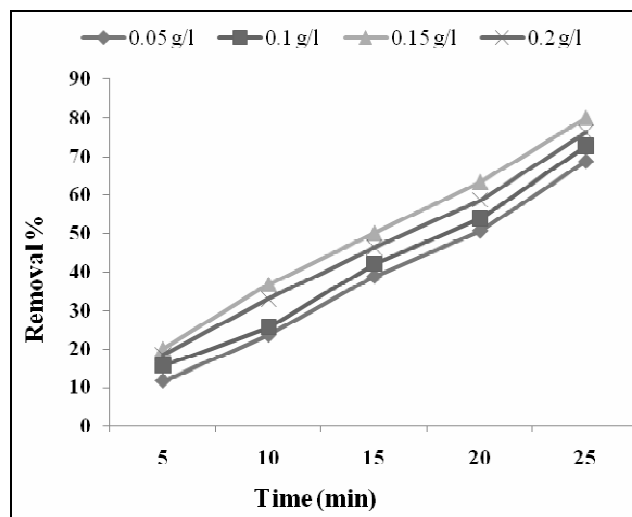


FIGURE 2 - Effects of ZnO dosage in UV/ZnO system (chlorpyrifos = 6 mg/L and pH=9).

3.2 Effect of irradiation time

The relationship between the photodegradation efficiency of chlorpyrifos and the irradiation time was investigated, and results are shown in Fig. 3. It can be seen

from Fig. 3 that the photodegradation efficiency of chlorpyrifos increases with an increase in irradiation time. When the illumination time increased from 5 to 25 min, the photodegradation efficiency of chlorpyrifos increased from 25 to 90%, and from 20 to 80% for UV/TiO₂ and UV/ZnO, respectively. It is believed that the photocatalytic degradation reaction of organic pollutants occurs on the surface of the catalyst, and O₂ and H₂O are necessary for the photocatalytic degradation. Under UV irradiation, electron-hole pairs are created on TiO₂ surface. Oxygen adsorbed on the catalyst surface prevents the recombination of electron-hole pairs by trapping electrons; superoxide radical ions ($\text{O}_2^{\cdot-}$) are thus formed, and $\cdot\text{OH}$ radicals are formed from holes reacting with either H₂O or OH⁻ adsorbed on the catalyst surface [17, 18].

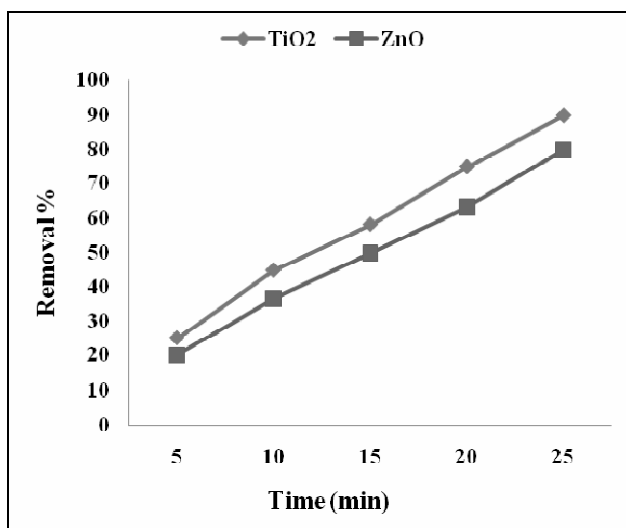


FIGURE 3 - Effect of illumination time on the photodegradation efficiency (TiO₂ = 0.15 g/L, ZnO = 0.15 g/L, pH = 9).

3.3 Effect of the initial pH

The effect of initial pH on photodegradation efficiency of chlorpyrifos is shown in Figs. 4 and 5. The initial pH has an important influence on photodegradation efficiency of chlorpyrifos, which increases with increasing initial pH. When the initial pH increased from 5 to 9, the photodegradation efficiency of chlorpyrifos increased from 75.5 to 90% but 65.7 to 80% for UV/TiO₂ and UV/ZnO, respectively. It is reported that in the illuminated TiO₂ system, the effect of pH on the photocatalytic reaction is generally attributed to the surface charge of the catalyst [19]. The point of zero charge (pzc) for TiO₂ and ZnO is 6.3 and 9.0, respectively [20, 21]. At pH values lower than 6.3 or 9.0, the catalyst's surface is positively charged, whereas at higher pH values, it is negatively charged [22]. Electrostatic attraction or repulsion between the catalyst's surface and the organic molecule takes place, depending on the ionic form of the organic compound, i.e. anionic or cationic, which consequently enhances or inhibits the photodegradation efficiency, respectively.

It can be observed from Fig. 4 that alkaline media are favorable for the photocatalytic degradation of chlorpyrifos. The main reasons for enhancement of the efficiency are as follows: (i) when there exists a large quantity of OH⁻, the surface of the catalyst is negatively charged at higher pH values. It is favorable for holes to transfer from the inner part of granules to the surface. The elevated concentration of OH⁻ will increasingly scavenge photo-generated holes and concurrently yield highly oxidative $\cdot\text{OH}$ species. On the contrary, at low pH conditions, the catalyst's surface is positively charged and the degradation reaction mainly results from photogenerated holes, whose oxidizing ability is somewhat lower than that of $\cdot\text{OH}$ species [23]; (ii) the electrostatic attraction between the chlorpyrifos molecules and TiO₂ or ZnO is greater at alka-

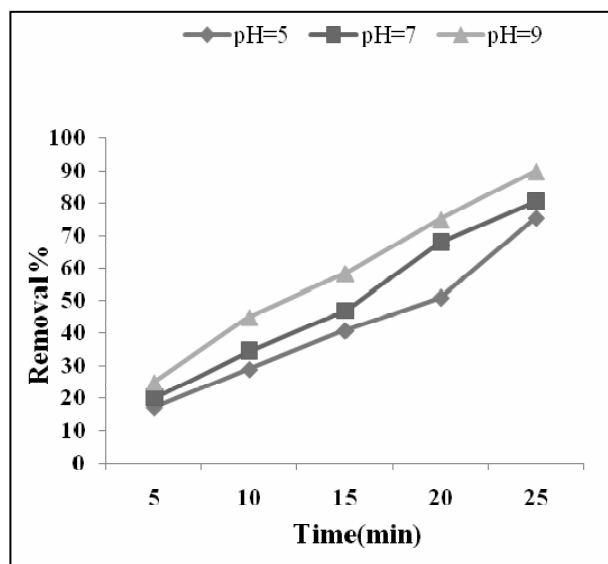


FIGURE 4 - Comparison of removal percentages in UV/TiO₂ system of chlorpyrifos at different pH values.

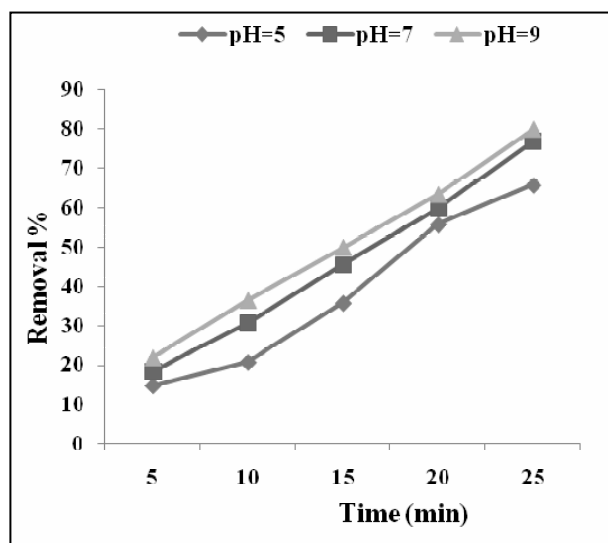


FIGURE 5 - Comparison of removal percentages in UV/ZnO system of chlorpyrifos at different pH values

line pH, so the chlorpyrifos molecules are allowed to reach the catalyst's surface easily [20, 23]. Therefore, they are more favorable for efficient generation of $\cdot\text{OH}$ and O^{2-} in an alkaline medium and achieve higher photodegradation efficiency.

3.5 Effect of the catalyst type

TiO_2 used the photodegradation was much faster in comparison to the reaction with ZnO (Fig. 6). TiO_2 has been suggested to be an efficient and viable photocatalyst for the degradation and mineralization of various organic pollutants, such as pesticides and other contaminants in water, in the presence of UV. The initial degradation rate of carbofuran with TiO_2 is higher than with ZnO . The higher rate of degradation over TiO_2 supports the view that the surface-mediated process is more predominant in the degradation reaction; thus, the higher surface area of TiO_2 ($55 \text{ m}^2 \text{ g}^{-1}$), compared to that of ZnO ($10 \text{ m}^2 \text{ g}^{-1}$), can be accounted for the higher rate of degradation over TiO_2 than ZnO (24-28). Similar results have been reported by Ahmed *et al.* [29], Devipriya and Yesodharan [30], and Rehman *et al.* [14]. The advantage of ZnO over TiO_2 is that it can absorb the desired pollutant over a broader UV spectrum and the corresponding threshold of ZnO is 425 nm. It is also suitable since its photodegradation mechanism has been proven to be similar to that of TiO_2 .

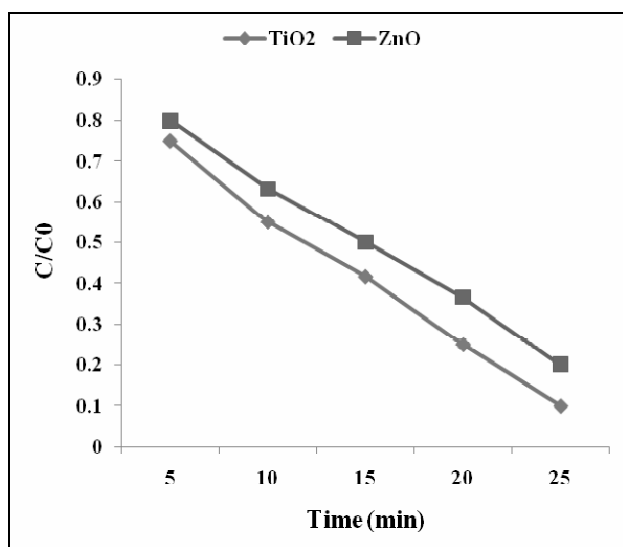


FIGURE 6 - Effect of catalyst type on removal percentage of chlorpyrifos in photocatalytic degradation.

3.6 Effect of NaHCO_3

A common inorganic ion, i.e. bicarbonate ion, was employed to study the photodegradation rate of chlorpyrifos. The influence of different concentrations of sodium bicarbonate (50-400 mg/L) on the photodegradation rate of chlorpyrifos is presented in Figs. 7 and 8. The decrease of the photodegradation efficiency of chlorpyrifos in the presence of bicarbonate ions is due probably to the hole scavenging properties of bicarbonate ions [20].

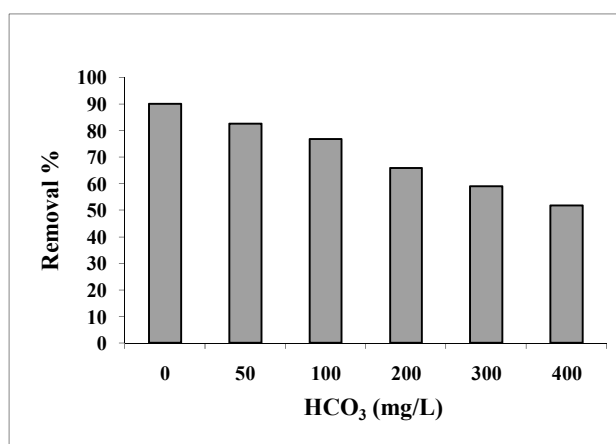


FIGURE 7 - Comparison of removal percentage of chlorpyrifos in the presence of bicarbonate in UV/ TiO_2 system ($\text{TiO}_2 = 0.15 \text{ g/L}$, pH = 9).

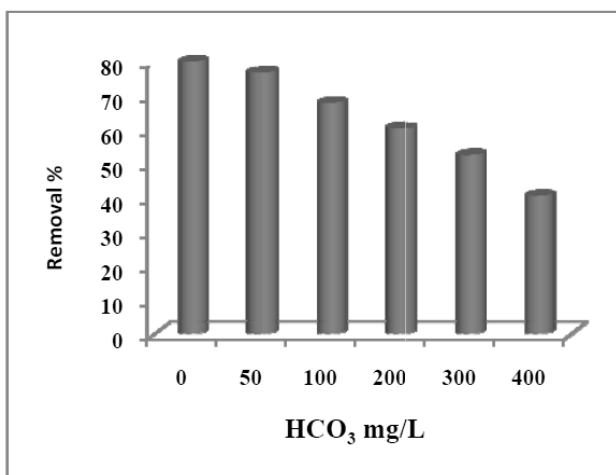


FIGURE 8 - Comparison of removal percentage of chlorpyrifos in the presence of bicarbonate in UV/ ZnO system ($\text{ZnO} = 0.15 \text{ g/L}$, pH = 9).

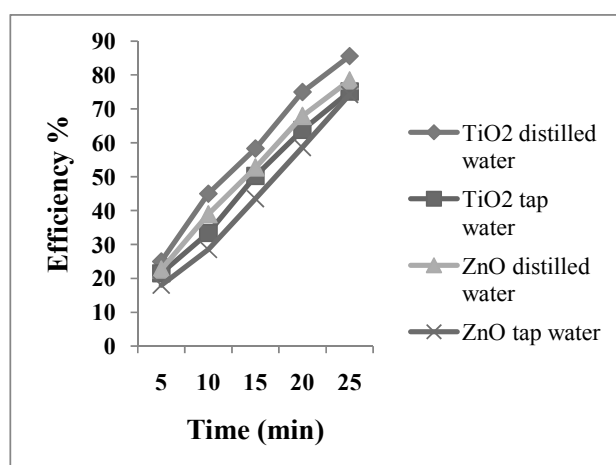


FIGURE 9 - Efficiency of UV/ ZnO and UV/ TiO_2 process for the degradation of chlorpyrifos from real water.

3.7 Photodegradation of chlorpyrifos in actual water

The actual water samples were obtained from drinking water in Shahrekord, Iran. The results (Fig. 9) indicate that the photodegradation rate is higher in distilled water

than in natural water. This inhibition is undoubtedly due to their ability to act as scavenger of hydroxyl radicals [31].

4 CONCLUSION

In the present work, the role of various operating parameters was explored and their effects on the photocatalytic degradation of chlorpyrifos. The results confirm that simultaneous presence of the catalyst and light is essential for photodegradation of organics in water. The results revealed that both ZnO and TiO₂ are effective for the removal of chlorpyrifos from water, and the latter proved to be superior with respect to the activity. The optimum catalyst loading was found to be 0.15 g L⁻¹. The photodegradation rate was higher in distilled water than in natural water. Semiconductors, such as TiO₂ and ZnO, are found to be efficient photocatalysts for the degradation of pesticides in water. Based on the results obtained herein, a general mechanism applicable for the photocatalytic degradation of a number of organic pollutants in water is proposed. The higher rate of degradation of chlorpyrifos in the presence of TiO₂, compared to ZnO, supports the hypothesis that the surface-mediated process is more prominent in the degradation reaction. TiO₂ has been suggested to be an efficient and viable photocatalyst for the degradation and mineralization of various organic pollutants, such as pesticides in water in the presence of UV, visible, or solar light.

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